

SCIENCE FOR CERAMIC PRODUCTION

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BLEACHING AND INTENSIFICATION OF SINTERING OF CERAMICS BASED ON IRON-BEARING CLAYS

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Bleached ceramics are produced on the basis of iron-bearing clays, and the process of its sintering is intensified. This ceramics has good technical and decorative properties, which is achieved by introducing into the mixture up to 20% CaCO₃ and 0.2% (above 100%) lithium chloride as a mineralizing additive.

The science of construction materials recognizes the important role of decorative and finishing materials in creating up-to-date architecturally expressive buildings, including their interior and exterior finishing. This is true of ceramic materials that have to meet stringent requirements imposed on technical and service properties (water absorption, strength, resistance to frost, etc.) and aesthetic properties (shape, color, texture, etc.).

The present study considers the production of bleached ceramic materials and products based on low-melting iron-bearing clays and the intensification of the sintering process.

The study was performed using clay from the Bol'shelogskoe and Vladimiskoe deposits in Rostov Region and the Gubskoe deposit in Krasnodar Region with different concentrations of iron oxides, with Fe₂O₃ content equal to 3.40, 5.32, and 5.52%, respectively (here and elsewhere, wt.%).

The ceramic mixtures also contained a high-calcium waste (HCW) material containing 5–20% CaCO₃ and li-

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TABLE 1

Material	Weight content, %								
	SiO ₂	Al ₂ O ₃	TiO ₂	Fe ₂ O ₃	CaO	MgO	R ₂ O	sulfates	calcination loss
Clay:									
Vladimiskoe	65.10	20.30	0.40	3.40	0.80	0.80	2.60	—	6.60
Bol'shelogskoe	65.06	10.09	—	5.32	—	—	7.58	0.17	11.78
Gubskoe	62.68	16.93	—	5.52	1.12	1.50	3.48	0.74	7.55
Vladimiskoe sand	97.50	2.61	—	0.54	—	—	—	—	1.34
Lithium-bearing waste* from Kamenskikhimvolokno JSC	—	—	—	0.04	0.01	—	0.10	0.20	—
High-calcium waste from Novocherkassk power plant	6.75	1.67	—	1.98	45.14	17.42	Traces	—	28.54
Ceramic mixtures**	56.67	14.80	0.28	2.43	9.58	4.04	1.82	—	10.46
	56.64	7.65	—	4.17	9.02	3.48	5.31	0.12	14.09
	54.97	12.44	—	4.31	9.82	4.53	2.44	0.52	11.13
Ceramic material based on the mixture	63.29	16.53	0.31	2.72	10.71	4.52	2.03	—	—
	65.93	8.81	—	4.86	10.51	4.06	6.18	0.14	—
	61.86	14.01	—	4.85	11.04	5.12	2.73	0.58	—

* The lithium-bearing waste contained 28.00–32.00% LiCl and 9.00% organic impurities.

** The mixtures contained different clays. Mixtures 1, 2, 3 contained 70% of Vladimiskoe, Bol'shelogskoe, and Gubskoe clay, respectively, plus 10% sand and 20% HCW.

thium-chlorine-bearing waste as the mineralizing additive in an amount of 0.2% (above 100%).

The chemical compositions of components, ceramic mixtures, and finished materials are listed in Table 1.

The samples were fired in an oxidizing medium at temperatures of 600–900°C with an interval of 100°C and a 1 h exposure at the maximum temperature. The technological and technical properties and colors of fired samples were determined (Table 2).

It can be seen from Table 2 that the color of all samples that do not contain CaCO_3 or contain CaCO_3 without the LiCl mineralizing additive is brown-pink or brown-red.

When a ceramic mixture contains simultaneously 20% CaCO_3 (or even 10% CaCO_3 if Bol'shelogskoe clay is used) and 0.2% LiCl, the color of samples varies from red-brown to white with a yellowish shade.

The technical and service parameters of the samples (water absorption, fire shrinkage, density, compression strength) decrease to some extent but remain quite acceptable for finishing decoration, especially for interior facing or for making fragmentary ornamental patterns for interior decoration, and meet the requirements of GOST 6141–91.

Therefore, ceramic mixtures containing iron-bearing low-melting clays and up to 20% calcium carbonate after firing yield a shrinkage-free material with increased water absorption and decreased strength. In order to intensify the process of sintering of ceramic mixtures, the lithium-chlorine-bearing waste was used, with LiCl content in the mixture equal to 0.2% (above 100%), which made it possible to produce ceramics with the required technical and service

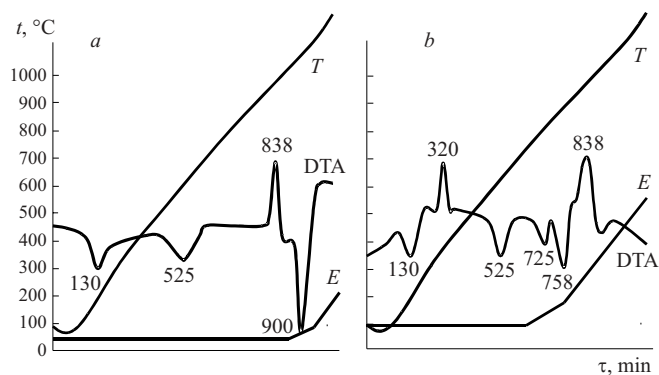


Fig. 1. Complex thermograms of ceramic mixtures V_1 (a) and V_3 (b) registering the third function, i.e., electric conductivity variation E .

parameters. The study of the specifics of solid-phase and liquid-phase sintering and bleaching of samples based on low-melting red-burning clays with an increased content of ferrous impurities revealed the physicochemical mechanism of the effect of $\text{CaCO}_3 + \text{LiCl}$ complex on these processes.

Differential thermal analysis together with recording of the electric conductivity variation in the firing of ceramics mixtures established the following (Fig. 1).

In firing mixture V_1 containing 20% CaCO_3 but without LiCl mineralizing agent, the DTA curve exhibits endothermic maxima at 130, 525, and 900°C corresponding to the removal of physical and crystallization moisture from the mixture, dehydration of kaolinite, and dissociation of CaCO_3 .

TABLE 2

Ceramic sample*	Weight content,** %			Water absorption, %	Fire shrinkage, %	Density, kg/m ³	Compressive strength, MPa	Color of ceramics
	clay	high-calcium waste***	lithium waste**** (above 100%)					
V_0	90	0	0	12.9	2.5	1914	35.3	Brown-pink
V_1	70	20	0	21.3	0.7	1608	22.9	Dark pink
V_2	80	10	0.2	17.6	1.8	1734	28.5	Pink-brown
V_3	70	20	0.2	20.7	0.9	1630	21.2	White with yellow shade
B_0	90	0	0	14.1	2.0	1884	33.8	Brown-pink
B_1	70	20	0	23.9	0.0	1570	21.9	The same
B_2	80	10	0.2	20.6	0.1	1674	22.6	White with yellow shade
B_3	70	20	0.2	24.5	0.0	1508	19.6	The same
G_0	90	0	0	13.4	2.3	1902	34.7	Brown-red
G_1	70	20	0	23.5	0.6	1602	22.3	Brown-pink
G_2	80	10	0.2	19.1	0.5	1702	23.4	Gray-pink with partial clarification
G_3	70	20	0.2	22.1	0.3	1518	20.1	White with yellow shade

* Ceramic samples V, B, and G are based on Vladimirscoe, Bol'shelogskoe, and Gubskoe clay, respectively.

** All compositions contained 10% Vladimirscoe sand.

*** Calculated on CaCO_3 .

**** Calculated on LiCl.

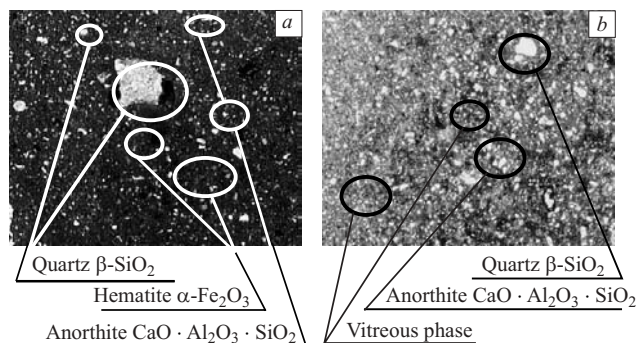
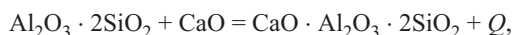


Fig. 2. Microstructure of ceramics samples made of mixtures V_1 (a) and V_3 (b) fired at 900°C (clear polished sections, $\times 10$, nickel II).

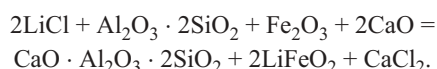
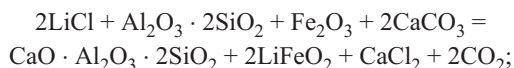
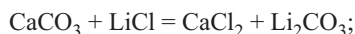
The exothermic maximum at 838°C is due to the formation of anorthite according to the following reactions:



which plays a significant structure-forming role in improving the mechanical strength of ceramics. A change in the electric conductivity of the mixture is registered only at the firing temperature around 900°C, which indicates the formation of a micromelt.

The integrated thermogram of ceramic mixture V_3 , which, in addition to 20% CaCO_3 , contains 0.2% LiCl , has a different form. Beside the endothermic maxima at 130 and 525°C, as in the previous thermogram an endothermic effect is registered at 725°C, which we identified in accordance with the conductivity curve variation as corresponding to the formation of a micromelt as the result of the reactions specified below, and an effect at 758°C corresponding to the dissociation of CaCO_3 . A decrease from 900°C to 758°C in the temperature of CaCO_3 dissociation is due to the catalytic effect of LiCl , as well as the influence of the emerging micromelt.

With the combination of LiCl and CaCO_3 in the mixture and in the presence of Fe_2O_3 , at a temperature above 600°C the following reactions proceed with the participation of metakaolinite, which is the product of dehydration of the argillaceous material:



In the course of these reactions low-melting compounds with the following melting temperatures are formed (°C): 607 for LiCl , 618 for Li_2CO_3 , and 782 for CaCl_2 . These reactions are responsible for the intensification of the sintering process with lowering of the temperature of CaCO_3 dissociation.

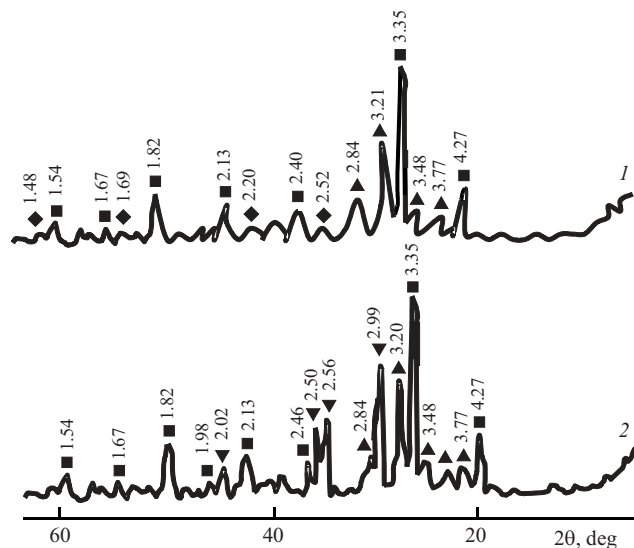


Fig. 3. Diffraction patterns of ceramic samples made of mixtures V_1 (1) and V_3 (2) fired at a temperature of 900°C: ■) quartz β - SiO_2 ; ♦) hematite α - Fe_2O_3 ; ▲) anorthite $\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$; ▼) fassaite $\text{Ca}(\text{Mg}, \text{Fe}^{3+}, \text{Al})[(\text{Si}, \text{Al})_2\text{O}_6]$.

tion, the formation of anorthite $\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$, and, most significantly, the formation of the melt at decreased temperatures.

The role of the micromelt is significant since its formation intensifies not only the solid-phase processes but the final sintering stage as well. Furthermore, the presence of the micromelt ensures the formation of low-melting iron-bearing LiFeO_2 compound that passes into the melt and dissolves Fe_2O_3 that has not reacted yet. The transition of iron oxides and other iron-bearing crystalline phases into the highly viscous aluminosilicate melt ensures its solidification in the vitreous state under cooling. X-ray phase analysis and nuclear gamma-resonance spectroscopy established [1] that Fe^{3+} ions in this case occupy tetrahedral positions and isomorphically replace aluminum ions according to the scheme $\text{Al}^{3+} \rightleftharpoons \text{Fe}^{3+}$.

The fixation of Fe^{3+} ions in the glass structure instead of the crystalline phases decreases the possibility of forming a charge transfer band that is the main factor of increasing whiteness and decreasing tinting in various silicate materials, which decreases by several orders of magnitude the light flux absorption and results in bleaching of high-iron ceramic mixtures.

The described mechanism of the physicochemical processes occurring in bleaching high-iron ceramics is convincingly substantiated by the results of petrographic studies and x-ray phase analysis.

A microscopic analysis of samples (Fig. 2) found that the ceramic structure contains colorless crystalline phases: β -quartz and anorthite $\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$. The ceramic based on mixture V_1 not containing the mineralizing agent LiCl contains as well a crystalline phase of hematite α - Fe_2O_3 , which is responsible for its red-brown color [2, 3].

In the sample made of mixture V_3 having a white color with a yellowish shade no crystalline iron-bearing phase has been identified, but an increased amount of the vitreous phase has been registered.

The x-ray phase analysis confirmed the presence of the same phases in ceramic samples V_1 and V_3 (Fig. 3). Sample V_3 contains a small quantity of fassaite $\text{Ca}(\text{Mg}, \text{Fe}^{3+}, \text{Al})[(\text{Si}, \text{Al})_2\text{O}_6]$ of a yellowish color.

Thus, in a ceramic mixture based on low-melting clay with a combined content of up to 20% CaCO_3 and 0.2% LiCl as the mineralizing agent, the process of ceramic sintering intensifies and the mixture becomes volumetrically fully

bleached due to the transition of $\alpha\text{-Fe}_2\text{O}_3$ (hematite), which imparts a red-brown color tint, into the vitreous phase, whose light absorption is significantly lower than that of the crystalline iron-bearing phases.

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